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Original scientific paper

Synthesis and characterization of a tetraaza macrocyclic ligand and its cobalt(II), nickel(II) and copper(II) complexes

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Abstract: Co(II), Ni(II), and Cu(II) complexes with a tetradentate nitrogen donor [N4] macrocyclic ligand, *viz.* 6,15-dimethyl-8,17diphenyl-7,16-dihydrodibenzo[*b*,*i*][1.4.8.11]tetraazacyclotetradecine, were synthesized. Their structures were determined based on elemental analyses, molar conductance and magnetic susceptibility measurements, and IR, ^{1}H-NMR (ligand) and electronic spectral studies. Based on analytical and molar conductance data, the complexes may be formulated as $[M(L)Cl_2]$ and $[M'(L)]Cl_2$ (where M = Co(II) and Cu(II), and M' = Ni(II)) due to their non-electrolytic and 1:2 electrolytic nature. Based on spectral studies, an octahedral geometry was assigned for the Co(II) complex, whereas square-planar and tetragonal geometry were proposed for the Ni(II) and Cu(II) complexes, respectively. The synthesized ligand and its complexes were screened for fungicidal activity against two pathogenic fungi (*i.e.*, *Fusarium moniliformae* and *Rhizoctonia solani*) to assess their growth inhibiting potential.

Keywords: tetraaza macrocycle; Co(II), Ni(II) and Cu(II) complexes; characterization.

INTRODUCTION

Transition metal complexes containing macrocycles are of considerable interest in terms of structural and coordination chemistry.[1] The chemical properties of macrocyclic complexes can be tuned to force metal ions to adopt unusual coordination geometries. Transition metal macrocyclic complexes have received much attention as an active part of metalloenzymes[2] and as biomimetic model compounds,[3,4] due to their resemblance to natural proteins such as hemerythrin and enzymes. Aza-type ligands appear very promising for potential use as antifertile, antibacterial, and antifungal agents as well as due to their other biological properties.[5–8] Transition metal complexes have received much attention as cata-

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lysts in oxidation and epoxidation processes.[9,10] Structural factors such as ligand rigidity, the type of donor atoms and their disposition have been shown to play significant roles in determining the binding features of macrocyclic ligands toward metal ions.[11,12] Due to the growing interest in macrocyclic ligands and their transition metal complexes, the synthesis, spectroscopic characterization and antifungal activities of Co(II), Ni(II), and Cu(II) complexes with a 14-membered macrocyclic ligand, *viz.* 6,15-dimethyl-8,17-diphenyl-7,16-dihydrodibenzo[*b*,*i*][1.4.8.11]tetraazacyclotetradecine (L), are reported in this paper. The preparation and structural formula of the ligand are shown in Fig. 1.

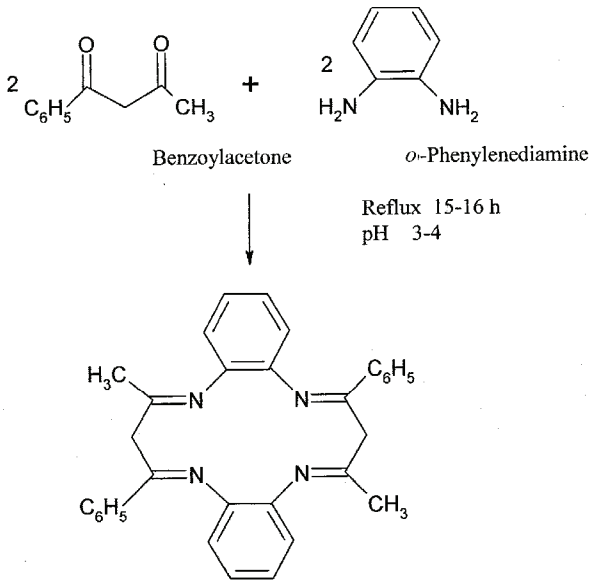

Fig. 1. Preparation and structural formula of the ligand.

EXPERIMENTAL

All the chemicals used were of analytical grade and procured from Sigma–Aldrich (USA) and Fluka (USA). The metal salts were purchased from E. Merck (Germany) and were used as received.

Synthesis of the ligand

A hot ethanolic solution (20 ml) of benzoylacetone (3.24 g, 0.020 mol) and an ethanolic solution (20 ml) of *o*-phenylenediamine (2.16 g, 0.020 mol) were mixed slowly under constant stirring. This mixture was refluxed at 85±5 °C for 15–16 h in the presence of a few drops of concentrated HCl (the pH was 3–4). On cooling, a yellow-coloured compound precipitated out. This was filtered, washed with cold EtOH, and dried under vacuum over P_4O_{10}. Yield: ≈75 %; m.p. 196 °C. Anal. Calcd. for $C_{32}H_{28}N_4$ (*FW* 468): C, 83.47; H, 6.08; N,13.91 %. Found: C, 83.52; H, 5.95; N, 13.86 %.

Synthesis of complexes

A hot ethanolic solution (20 ml) of the ligand (0.40 g, 0.0010 mol) and an ethanolic solution (20 ml) of the required metal salt ($CoCl_2 \cdot 6H_2O$, $NiCl_2 \cdot 2H_2O$ or $CuCl_2 \cdot 2H_2O$) (0.0010 mol) were mixed together under constant stirring. This reaction mixture was refluxed at 80–85 °C for 4 h. On cooling, the corresponding coloured complex separated out, which was filtered, washed and recrystalized from 50 % ethanol and dried under vacuum over P_4O_{10}.

Physical measurements

The C and H contents were determined on a Carlo-Erba 1106 elemental analyzer (C. D. R. I. Lucknow, India). The N content of the complexes was determined using the Kjeldhal method.[13] The metal contents were determined by volumetric analysis.[14] The molar conductance values were measured on an Elico (CM82T) conductivity bridge at 298 K in acetonitrile. The magnetic susceptibility values were measured at room temperature on a Gouy balance using $CuSO_4 \cdot 5H_2O$ as the calibrant. Corrections for diamagnetism were realised using Pascal constants.[15] The ^{1}H-NMR spectra were recorded on a Hitachi FT–NMR model R-600 spectrometer using $CDCl_3$ as the solvent. The chemical shifts are given in ppm relative to tetramethylsilane. The IR spectra were recorded as KBr pellets on a FTIR Spectrum BX-II spectrophotometer. The electronic spectra were recorded in acetonitrile on a Shimadzu UV mini--1240 spectrophotometer. The EPR spectra of the complexes were recorded as polycrystalline samples in acetonitrile solution, at liquid nitrogen temperature for Co(II) and at room temperature for the Cu(II) complex using an E4 EPR spectrometer employing DPPH as the g-marker.

Antifungal screening

The *in vitro* antifungal activities of the ligand and its complexes were tested against the pathogenic fungi *Fusarium moniliformae* and *Rhizoctonia solani* using the food poison technique.[16-20] The percent inhibition was measured according to the formula:

$$\% \text{ Inhibition} = 100(C–T)/C$$

where C and T are the radial diameter of the colony in the control and the treated, respectively.

RESULTS AND DISCUSSION

Based on elemental analyses, the complexes were assigned the compositions shown in Table I. The Co(II) and Cu(II) complexes were non-electrolytes with conductance values of 8–12 S cm^2 mol^{-1} in acetonitrile. However, the molar conductance value of the Ni(II) complex in acetonitrile was 202 S cm^2 mol^{-1}, indicating a 1:2 electrolytic nature (the literature range in acetonitrile is 200–300 S cm^2 mol^{-1}).[21] Thus, these complexes may be formulated as $[M(L)Cl_2]$ and $[M'(L)]Cl_2$, where M = Co(II) or Cu(II) and M' = Ni(II), L = 6,15-dimethyl-8,17-diphenyl-7,16-dihydrodibenzo[*b*,*i*][1.4.8.11]tetraazacyclotetradecine.

The ^{1}H-NMR spectrum of the ligand (L) gave no signal corresponding to primary amine protons. This suggests the derivatization of carbonyl groups. A multiplet in the δ range 2.20–2.64 ppm may be attributed to the imine methyl and methylene protons of benzoyl acetone (6H, CH_3–C=N and 4H, N=C–CH_2–C=N, respectively). Another multiplet in the δ range 7.28–7.52 ppm is assigned to aromatic ring protons.[22]

TABLE I. Yield, molar conductance (Λ_M) in acetonitrile, elemental analysis data and some physical properties of the prepared complexes (L = 6,15-dimethyl-8,17-diphenyl-7,16-dihydrodibenzo[*b*,*i*]1.4.8.11][tetraazacyclotetradecine)

Complex	Λ_M / S^1 cm^2 mol^{-1}	Colour	M.p. °C	Yield %	Found (Calcd.), %			
					M	C	H	N
$[Co(L)Cl_2]$	8	Shiny	278	66	9.84	64.43	4.78	9.34
$C_{32}H_{28}CoN_4Cl_2$		pink			(9.87)	(64.32)	(4.69)	(9.38)
$[Ni(L)]Cl_2$	202	Shiny	292	71	9.83	65.40	4.64	9.44
$C_{32}H_{28}NiN_4Cl_2$		red			(9.88)	(65.34)	(4.68)	(9.39)
$[Cu(L)Cl_2]$	12	Bluish	284	73	9.42	63.62	4.62	9.32
$C_{32}H_{28}CuN_4Cl_2$		green			(9.46)	(63.83)	(4.65)	(9.30)

The IR spectrum of the free ligand exhibited no bands corresponding to a free primary diamine or a free keto group. This suggests complete condensation of the amino groups with the keto groups.[23] The bands at 1594 and 1566 cm^{-1} were due to ν(C=N) vibrations of the phenyl, and methyl, groups, respectively. The strong and sharp absorption bands appearing in the regions 2800–3049 and 1402–1466 cm^{-1} in the spectra of all of the complexes may be due to C–H stretching and bending vibrations, respectively.[24] On complexation, the position of the ν(C=N) band shifted by 18–34 cm^{-1} to lower wavenumbers. This indicates coordination through the N atoms of the imine groups.[25]

At room temperature, the Co(II) and Cu(II) complexes showed magnetic moments of 4.86 and 1.99 μ_B, corresponding to 3 and 1 unpaired electrons, respectively, while the Ni(II) complex was diamagnetic as expected for a square-planar d^8 system[26] (Table II).

TABLE II. Magnetic moments at room temperature (μ_{eff}) and electronic spectral data of the complexes (L = 6,15-dimethyl-8,17-diphenyl-7,16-dihydrodibenzo[*b*,*i*][1.4.8.11]tetraaza-cyclotetradecine)

Complex	μ_{eff} / μ_B	λ_{max} / nm	ε / dm^3 mol^{-1} cm^{-1}
$[Co(L)Cl_2]$	4.86	830	55
		677	69
		532	90
$[Ni(L)]Cl_2$	Diamagnetic	735	49
		478	87
		402	127
$[Cu(L)Cl_2]$	1.99	876	52
		534	65
		356	153

The electronic spectrum of the Co(II) complex exhibited absorption bands at 830, 677 and 532 nm, which may be assigned to the transitions $^4T_{1g}(F) \rightarrow$ $\rightarrow$ $^4T_{2g}(F)$ (ν_1), $^4T_{1g} \rightarrow {}^4A_{2g}$ (ν_2) and $^4T_{1g}(F) \rightarrow {}^4T_{2g}(P)$ (ν_3), respectively.[27] The Ni(II) complex displayed an electronic spectrum with transitions at 735, 478

and 402 nm. These bands may be assigned to the transitions $^1A_{1g} \rightarrow {}^1A_{2g}(G)$ (ν_1), $^1A_{1g}(D) \rightarrow {}^1B_{2g}(G)$ (ν_2) and $^1A_{1g}(D) \rightarrow {}^1E_g(G)$ (ν_3), respectively.[28] The Cu(II) complex displayed bands at 876 nm and 534 nm, which may be assigned to the transitions $^2B_{1g} \rightarrow {}^2A_{1g}$ ($d_{x^2-y^2} \rightarrow d_{z^2}$) ($\nu_1$), $^2B_{1g} \rightarrow {}^2B_{2g}$ ($d_{x^2-y^2} \rightarrow d_{zy}$) ($\nu_2$). The third band at around 356 nm may be due to charge transfer[29] (Table II).

The EPR spectrum of the Co(II) complex (Table III) was recorded as a polycrystalline sample and in acetonitrile solution at liquid nitrogen temperature (77 K). In both cases, the *g*-values were almost identical. The large deviation in g values from the free electron value (g = 2.0023) is due to a large angular momentum contribution. The EPR spectrum of the Cu(II) complex was recorded at 300 K as a polycrystalline sample and in acetonitrile solution, on the X-band at the frequency of 9.3 GHz under a magnetic field strength 3400 G. The polycrystalline spectrum showed a well-resolved anisotropically broad signal. The analysis of the spectra give $g_\parallel$ 2.08–2.11 and $g_\perp$ 2.02–2.08 (Table III). The trend $g_\parallel > g_\perp >$ > 2.0023 observed for the complex under study indicates that the unpaired electron is localized in the $d_{x^2-y^2}$ orbital of the Cu(II) ion.[30] Based on the spectral studies, the following geometries may be suggested for the complexes (Fig. 2).

TABLE III. EPR spectral data of the complexes (L = 6,15-dimethyl-8,17-diphenyl-7,16-dihydrodibenzo[*b*,*i*][1.4.8.11]tetraazacyclotetradecine)

Complex	*T* / K	Polycrystalline			DMSO solution	
		$g_\parallel$	$g_\perp$	g_{iso}	$g_\parallel$	$g_\perp$
$[Co(L)Cl_2]$	77	2.3387	2.0174	2.1245	2.3294	2.0052
$[Cu(L)Cl_2]$	298	2.1182	2.0269	2.0842	2.0834	2.0890

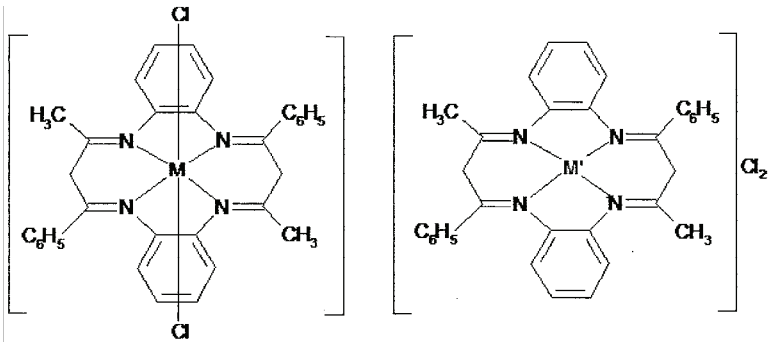

Fig. 2. Suggested geometries of the complexes, where M = Co(II) and Cu(II), and M' = Ni.

Antifungal screening

The results of the antifungal screening showed that the tested complexes exhibited higher activities than the ligand towards the inhibition of the test fungi under the *in vitro* test conditions. The minimum inhibitory concentration (*MIC*) of the test compounds against both fungi was 500 ppm, at which concentration

100 % inhibition was observed. The compounds showed fungal inhibition in the following order: benzoylacetone< *o*-phenylenediamine < L< Ni(II) complex < Cu(II) complex < Co(II) complex (Table IV).

TABLE IV. Fungicidal screening data of the ligand and complexes at 125 and 250 ppm concentrations after 8 days at 30±2 °C (L = 6,15-dimethyl-8,17-diphenyl-7,16-dihydrodibenzo[*b,i*][1.4.8.11]tetraazacyclotetradecine)

Compound	Fungal inhibition, %			
	F. moniliformae		*R. solani*	
	125	250	125	250
Benzoylacetone	32	45	35	49
o-Phenylenediamine	47	59	52	61
L	54	66	56	70
$[Co(L)Cl_2]$	67	82	71	83
$[Ni(L)]Cl_2$	61	72	63	75
$[Cu(L)Cl_2]$	63	75	68	79
Standard (mancozeb)	82	84	85	86

CONCLUSIONS

The present study revealed octahedral, square-planar and tetragonal geometry for the Co(II), Ni(II) and Cu(II) complexes, respectively. The ligand acts in a tetradentate manner coordinating through four nitrogens of the azomethine groups in an N N N N fashion. Moreover, the fungicidal data revealed that the complexes were superior to the free ligand in the inhibition of the tested fungi. It is proposed that concentration plays a vital role in increasing the degree of inhibition; the activity increased with increasing concentration of the complexes.

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И З В О Д

СИНТЕЗА И КАРАКТЕРИСАЊЕ ТЕТРААЗА МАКРОЦИКЛИЧНОГ ЛИГАНДА И ЊЕГОВИХ КОБАЛТ(II)-, НИКЛ(II)- И БАКАР(II)- КОМПЛЕКСА

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Синтетизовани су Co(II), Ni(II) и Cu(II) комплекси са макроцикличним лигандом са тетрадентатним азотним донором (N_4), као што је 6,15-диметил-8,17-дифенил-7,16дихидродибензо[*b,i*][1.4.8.11]тетраазациклотетрадецин. Њихове структуре су одређене на основу елементалне анализе, мерења електричне моларне проводљивости и магнетне сусцептибилности, као и ИЦ, ^{1}H-NMR (лиганд) и електронских спектара. Према аналитичким подацима и моларној електричној проводљивости, а због њихове неелектролитичке или 1:2 електролитичке природе, комплекси могу да се формулишу као $[M(L)Cl_2]$ и $[M'(L)]Cl_2$ (где су M = Co(II), Cu(II) и M' = Ni(II)). На основу спектралних проучавања комплексу Co(II) приписана је октаедарска геометрија, док је за Ni(II) и Cu(II) предложена квадратно-планарна и тетра-

гонална геометрија. Испитивана је и активност синтетизованог лиганда и његових комплекаса према две патогене гљивице (*Fusarium moniliformae* и *Rhizoctonia solani*) да би се утврдило њихово инхибиторско деловање.

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